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# RESIDUAL PARAMAGNETISM OF COBALT IN SOME COBALT (III) COMPLEXES

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**ABSTRACT.** Second order paramagnetic term and electronicabsorp tion spectra of cobalt (III) in fifteen octahedral cobalt (III) complexes have been measured by the Gouy method and a UVISPECK. The observed values of residual paramagnetism are found to be always lower than those calculated on the basis ofl igand field theory. Probable explanations for the observed discrepancy are presented. The nature of the bonding in these complexes are also discussed.

## INTRODUCTION

The magnetic properties of spin-paired cobaltic complexes have received rather little attention. The early works indicate that the observed susceptibilities of octahedral cobalt (III) complexes have a substantial contribution due to the second order paramagnetism term which is independent of temperature (Rosenbohm, 1919; Kernahan *et al*, 1955; Belova *et al*, 1955; Ballhausen *et al*, 1957; Kanekar *et al*, 1966). Ballhausen and Asmusen (1957) have shown that second order paramagnetism term is highly dependent upon the nature of the ligands and follows the spectrochemical series very closely. The interest in the magnetic properties of cobalt (III) complexes has arose recently owing to the recent development of the ligand field theory (Grifith *et al*, 1957).

It is wellknown that oxidation from $Co^{+2}$ to $Co^{+3}$ results in the increase of $\Delta E$ values and as a consequence the spins are paired in an octahedral environment of $3d^6$ cobalt (III) and cobaltic complexes are generally found to be diamagnetic. But there still remains some contribution of the second order paramagnetism of the cobalt atom. Grifith and Orgel (1957) were the first to calculate theoretically, on the basis of ligand field theory, the amount of second order paramagnetism in octahedral spin-paired complexes of $d^6$ system. With an end in view to check the validity of Grifith and Orgel's theory, we have measured the room temperature magnetic susceptibility as well as the electronic absorption spectra of some cobalt (III) complexes. The preparation and characterisation of a large number of cobaltic complexes containing biguanide and 1-amidino-0-alkylurea as the basic units have already been reported from this laboratory (Dutta *et al*, 1964, 1965, 1967). It may be mentioned here that this is the first report on the determination of second order paramagnetism term of cobalt (III) heterochelates.

## EXPERIMENTAL

The complexes were prepared according to the published procedures (Dutta *et al*, 1965; Dutta *et al.*, 1965, 1967; Ray *et al.*, 1938, 1940) and their purity was checked by elemental analysis of metal and nitrogen.

Magnetic susceptibility measurements in the state of powder were carried out by modified Gouy method. The forces on the samples were recorded by a single pan semimicro Mettler analytical balance reading upto fifth decimal place of a gram. Copper sulphate pentahydrate was used as the calibrant.

Electronic absorption spectra in state of aqueous solution were recorded with the help of a Hilger-Watts Uvispeck Spectrophotometer using one cm. cells.

Chemicals used were all G.R.E. Merck variety.

## RESULT

The following diamagnetic corrections were utilised to calculate $\chi_D$ : Co $=-10$; N (open chain) $=-5.56$; N(ring) $=-4.6$; NO $=-13.1$; NO $=-18.9$; $Cl^- = 20.1$; $I^- = 44.6$; S $=-15$; $NH_3 = -17.1$; H O $=-12.8$; ophen $=-105$; dipy $=-101$.

The observed $\chi$ was calculated by the relation (van Vleck, 1932) :

$$\chi_p + \chi_D = \chi_M$$

where $\chi_D$ = diamagnetic susceptibility of the atoms,

$\chi_M$ = molar susceptibility in C.G.S. unit.

and $\chi$ (calcd) was obtained by using observed $K$ values in equation 1). The results so obtained are included in table 1.

## DISCUSSION

Residual paramagnetism can arise from either (i) second order paramagnetism or (ii) quenching of diamagnetism or both. Recent work of Proctor *et al* (1951) discards the quenching of diamagnetism factor as a possible source of residual paramagnetism. The diamangetism of the ligands is retained in the complex and is not quenched.

According to the ligand field theory of Grifith and Orgel (1957) we may also calculate $\chi$ values from the relation :

$$\chi_p = \frac{2}{3} N \left[\frac{eh}{2mC}\right]^2 \cdot \frac{24}{K} = \frac{4.085}{K} \quad .. \quad (1)$$

where $K$ denotes the energy separation in wave number unit between the ground state ($^1A_{1g}$) and the excited singlet state ($^1T_{1g}$) of O symmetry cobalt(III) complexes.

Table 1

Magnetic susceptibility data of cobalt (III) complexes

| Compound | (K, $cm^{-1}$)* $^1T_{1g} \leftarrow {}^1A_{1g}$ | $X_a$** | $X_M$ | $X_D$ | $X_p$ (obs.) | $X_p$ (calcd.) | Orbital reduction factor, $k$ |
|---|---|---|---|---|---|---|---|
| 1. $[Co(BigH)_3](SO_4)_{1\cdot5}.3.5H_2O$ | 20,900 | $-0.034 \pm 0.0002$ | 19.6 | 174.6 | 155 | 195.4 | 0.7 |
| 2. $[Co(AP^iUH)_2](SO_4)_{1\cdot5}2.5H_2O$ | 20,800 | $-0.056 \pm 0.0008$ | 38 | 185 | 147 | 196.3 | 0.8 |
| 3. $[Co(BigH)_2(ophen)]Cl_3$ | 21,200 | $-0.186 \pm 0.0004$ | 102.4 | 234.4 | 132 | 192 | 0.7 |
| 4. $[Co(BigH)_2(dipy)]Cl_3.3H_2O$ | 21,400 | $-0.224 \pm 0.003$ | 133 | 268 | 135 | 191 | 0.7 |
| 5. $[Co(BigH)_2(AEUH)]Cl_3.0.5H_2O$ | 21.000 | $-0.052 \pm 0.0004$ | 262 | 171.2 | 145 | 194 | 0.8 |
| 6. $[Co(en)_2(BigH)]I.SO_4$ | 20,800 | $-0.075 \pm 0.0008$ | 38.0 | 188.0 | 150 | 196 | 0.8 |
| 7. $[Co(AMUH)_2(BigH)]I_3$ | 20,800 | $-0.055 \pm 0.0005$ | 42.5 | 218.5 | 176 | 196 | 0.9 |
| 8. $[Co(AMUH)_2(AEUH)]I_3.H_2O$ | 20,700 | $-0.005 \pm 0.0008$ | 45 | 227 | 182 | 188 | 1.0 |
| 9. $[Co(NH_3)_2(AMUH)_2](SO_4)_{1\cdot5}.2H_2O$ | 20,200 | $\pm 0.137 \pm 0.003$ | 69 | 128 | 197 | 202 | 1.0 |
| 10. $[Co(Py)_2(AEUH)_2](NO_3)_3$ | 20,200 | $-0.032 \pm 0.0003$ | 20.6 | 190.6 | 170 | 202 | 0.9 |
| 11. $Cis[Co(NO_2)_2(ABIUH)_2]NO_2$ | 22,000 | $\pm 0.064$ | 32.5 | 147.5 | 180 | 188 | 1.0 |
| 12. $trans\ [Co(NO_2)_2(ABiUH)_2]NO_2$ | 21,500 | $+0.044 \pm 0.0005$ | 22.5 | 147.5 | 170 | 190 | 0.9 |
| 13. $[Co(AMUH)_2(ophen)]Cl_3.6H_2O$ | 21,150 | $-0.152 \pm 0.003$ | 104 | 279 | 175 | 193 | 0.9 |
| 14. $[Co(AMUH)_2(dipy)]Cl_3.7H_2O$ | 21.150 | $-0.171 \pm 0.002$ | 116 | 288 | 172 | 193 | 0.9 |
| 15. $[Co(AMUH_3(en\ ](SO_{4\ 1\cdot5}.5H_2O$ | 20,800 | $\pm 0.033 \pm 0.0004$ | 19.2 | 160.8 | 180 | 196 | 0.9 |

** where max values are in a range, the mean value was taken for simplicity.

** $X$ denotes the susceptibility per gm.

[BigH = biguanide ; ophen = ortho-phenanthroline ; dipy = 2-2′-dipyridyl ; en = ethylenediamine ; py = pyridine ; AMUH = 1-amidino-O-methylurea ; AEUH = 1-amidino-O-ethylurea ; AP UH = 1-amidino-O-isopropylurea ; ABIUH = 1-amidino-O-isobutylurea.]

The observed values for residual paramagnetism are found to be always lower than those calculated theoretically. This discrepancy probably reflects bounding effects on the susceptibility of these complexes. Uncertainties in the calculation of diamagnetic susceptibility of the atoms cannot be overlooked too.

Orbital reduction factor, $k$ was calculated from the ratio $\chi$ (obs.)/$\chi$ (calcd.) and is recorded in table 1. The results indicate that $k$ varies from 0.7 to 1.0 in close agreement with the work of Ballhausen *et al* (1957).

According to Grifith and Orgel (1957), the error in calculating $\chi$ values should be within 20%, but in our case the error is about 30%. This is presumably due to uncertainties in the calculation of diamagnetic susceptibility of the atoms. Thus this study clearly reflects the validity of Grifith and Orgel's theoretical treatment of ligand field theory.

Magnetic susceptibility measurements indicate that the complexes are essentially diamagnetic. Hence the complexes are octahedral and are formed involving the use of $d^2sp^3$ hybrid orbitals for bonding. If the complexes would have been formed utilising $sp^3d^2$ hybrid orbitals, a moment value corresponding to two unpaired electrons should have been recorded. Furthermore, biguanides, 1-amidino-0-alkylureas, ortho-phen-anthroline, 2-2′-dipyridyl, ethylenediamine etc. are strong field ligands and formation of high spin complexes are precluded. The inner orbital nature of the complexes has also been demonstrated from their spectral characteristic. All the complexes exhibit two ligand field bands corresponding to the transitions, $^1T_{1g} \rightarrow {}^1A_{1g}$ and $^1T_{2g} \rightarrow {}^1A_{1g}$ typical of octahedral cobalt (III) complexes (Busch, 1960; Cotton *et al*, 1962).

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